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NWC TP 6619

**Effects of Surface Interactions and Mechanical  
Properties of Plastic Bonded Explosives  
on Explosive Sensitivity.  
Part 2: Model Formulation**

by  
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and  
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**MARCH 1985**

**NAVAL WEAPONS CENTER  
CHINA LAKE, CA 93555-6001**



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### FOREWORD

There is a need to reduce the explosive sensitivity of explosives and propellants without sacrificing their energy. We found that the impact sensitivities of some explosives can be changed by surface modification. Propellant studies have also shown that microstructural damage and dewetting have a significant effect on the mechanical properties of the propellant. This study is to investigate the correlation between explosive sensitivity and surface interaction between binder and explosive, and between chemical and mechanical properties of binder and explosive formulation.

Correlations have been found in the model formulations between the interfacial bond energies measured in the surface studies and the stresses at the onset of dewetting.

This work is funded as a joint effort between the Office of Naval Research (ONR) (Code 432) and Naval Sea Systems Command (NAVSEA) (62R32). The ONR effort is under Task Numbers AARR024-02 and AARR014-11 with R. S. Miller as the technical monitor. The NAVSEA effort is under Task Number SR02403 with G. Edwards and H. Adolph as the project managers.

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Released for publication by  
B. W. Hays  
*Technical Director*

NWC Technical Publication 6619

Published by . . . . . Technical Information Department  
Collation . . . . . Cover, 14 leaves  
First printing . . . . . 185 copies

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM									
1. REPORT NUMBER NWC TP 6619	2. GOVT ACCESSION NO. AD-A157900	3. RECIPIENT'S CATALOG NUMBER									
4. TITLE (and Subtitle)  EFFECTS OF SURFACE INTERACTIONS AND MECHANICAL PROPERTIES OF PLASTIC BONDED EXPLOSIVES ON EXPLOSIVE SENSITIVITY. PART 2: MODEL FORMULATION		5. TYPE OF REPORT & PERIOD COVERED Annual 1 Oct 1983-30 September 1984									
		6. PERFORMING ORG. REPORT NUMBER									
7. AUTHOR(s)  Rena Y. Yee and E. C. Martin		8. CONTRACT OR GRANT NUMBER(s)									
9. PERFORMING ORGANIZATION NAME AND ADDRESS  Naval Weapons Center China Lake, CA 93555-6001		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS  PE 61153N, See foreword for other information									
11. CONTROLLING OFFICE NAME AND ADDRESS  Naval Weapons Center China Lake, CA 93555-6001		12. REPORT DATE March 1985									
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 26									
		15. SECURITY CLASS. (of this report)  UNCLASSIFIED									
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE											
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution is unlimited.											
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)											
18. SUPPLEMENTARY NOTES											
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)											
<table border="0"> <tr> <td>Dilatation</td> <td>Explosives</td> <td>Polymer Crystallinity</td> </tr> <tr> <td>Energetic Polymers</td> <td>Ignition Characteristics</td> <td>Explosive Sensitivity</td> </tr> <tr> <td>Explosive Sensitivity</td> <td>Mechanical Properties</td> <td>Surface Interactions</td> </tr> </table>			Dilatation	Explosives	Polymer Crystallinity	Energetic Polymers	Ignition Characteristics	Explosive Sensitivity	Explosive Sensitivity	Mechanical Properties	Surface Interactions
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(U) *Effects of Surface Interactions and Mechanical Properties of Plastic Bonded Explosives on Explosive Sensitivity; Part 2: Model Formulation*, by Rena Y. Yee and E. C. Martin. China Lake, Calif., Naval Weapons Center, March 1985. 26 pp. (NWC TP 6619, publication UNCLASSIFIED.)

(U) Eight major mixes were prepared from three baseline binders. The tensile and torsional shear mechanical properties and burning behavior of these model mixes have been investigated. The binder-filler bond energy determined from the surface studies can be correlated to the energy required for the onset of dewetting. The specific impulses of the model mixes were calculated. Some of the model mixes containing energetic binder were difficult to ignite at low energy flux. This suggests that the formulations may be candidates for insensitive energetic systems.

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## ACKNOWLEDGMENT

The authors would like to acknowledge the technical contributions of various coworkers at the Naval Weapons Center. Albert H. Lepie, Herbert P. Richter and Alan L. Woodman measured the mechanical properties. Alice I. Atwood and Donald E. Zurn performed the burn rates and ignitability determinations. Various members of the Naval Weapons Center's Explosive Formulation Branch assisted in the formulation preparations. Alan L. Woodman was very helpful in editing.

The valuable suggestions of Russell Reed, May L. Chan, Thomas L. Boggs, Carl L. O'Neal and Albert A. DeFusco are appreciated. We would also like to thank R. S. Miller of ONR and H. Adolph of NAVSEA for their technical guidances.

## INTRODUCTION

Plastic bonded explosives (PBX) are mechanical mixtures of explosive crystals with polymeric binders and in some cases plasticizers. Different sensitivity parameters are used to characterize the reaction of explosives toward impact, friction, temperature, and electric discharge. There is a need to reduce the explosive sensitivity without sacrificing energy. The literature suggests that surface properties play a role in desensitization (Reference 1). We have found that the impact sensitivities of some explosives can be changed by surface modification (Reference 2). Other investigations revealed that the PBX impact sensitivity is related to its viscoelastic dynamic energy loss (Reference 3). Propellant studies at the Naval Weapons Center (NWC) showed that microstructural damage and dewetting have a significant effect on the mechanical properties of the propellant (References 4 through 6). Similar effects can be expected to occur in a PBX in that the presence of voids and microcracks due to interfacial debonding, dewetting, and formation of reactive free radicals by molecular bond scission is expected to affect the explosive sensitivity. To determine the influence of these factors, the surface properties of binders and fillers were determined (References 7 and 8). The surface properties of binders have been determined in both the uncured and cured states (Reference 9), and the surface properties of some explosive crystals have been characterized in an earlier program (Reference 10).

Model explosive formulations were prepared using selected binders and cyclotrimethylenetrinitramine (RDX). The surface interactions were determined by microscopic examination, dilatation measurements, and surface free energy studies. The NWC propellant damage energy concept will be applied to define the damage properties and their relation to sensitivity (Reference 3).

Experimental specimens from the model formulations were sent to Dr. R. Martinson, Lockheed, Palo Alto Laboratory, Palo Alto, Calif. (small angle X-ray and photo acoustic studies), to Prof. J. T. Dickinson, Washington State University (WSU), Pullman, Wash. (fracto-emission studies), and Prof. K. Kuo, Pennsylvania State University (PSU), University Park, Penn. (ignition properties). The results obtained by these investigators will be included in the correlation studies.

## DISCUSSION

## MODEL FORMULATIONS

In the beginning of the program, several binders were selected that are representative of those currently being used in the propellant and explosive area (Reference 8). The binders being used to establish a data base include hydroxy-terminated polybutadiene/isophorone diisocyanate (R45M/IPDI), acrylic polymer, poly(glycidyl azide) (GAP), and bis(azido)methyl oxetane/tetrahydrofuran (BAMO/THF).

The energetic fillers are cyclotetramethylenetetranitramine (HMX) and RDX. RDX will be used in the first phase of model formulation.

The model formulations are designed to compare surface interactions and mechanical properties. In order to have similar binder/solid interface for all mixes, the particle size distribution and volume percent of solid have been kept constant. The particle size distribution of RDX is kept constant by using the same ratio of two lots of RDX for all mixes. One lot is a Class A RDX screened through a No. 100 Tyler sieve (149 microns) to remove larger particles and the other lot is a Class E RDX. Since the density of the binder varies, the volume percent of RDX is kept constant by changing the weight percent of RDX (calculated from the density of the binder).

Eight major mixes have been prepared from three of the baseline binders. The status of the various specimens is given in Table 1.

The binder/plasticizer ratio and additive contents are very critical in these energetic systems. A number of hand mixes were made to approximate the ratios of the ingredients in order to get a rough check on the physical properties. However, when scaled up to full-size mixes where more accurate ingredient ratios can be obtained, some of the mixes (BLX-7, BLX-10) had inferior properties.

The composition of each mix is listed in Tables 2 through 5.

## TENSILE AND TORSIONAL SHEAR PROPERTIES

The tensile data were obtained from end-bonded specimens (1 by 1 by 7.6 cm) (Reference 3). The torsional shear data were obtained in a shear dilatometer designed at NWC (Reference 4). The specimens were of the same configuration but not end bonded.

A typical torsional shear stress-strain curve and volume dilatation curve are shown in Figure 1. The onset of dewetting is defined as the point at which the volume dilatation is equal to 0.1%. The

TABLE 1. Sample Status.

Mix No.	Binder system	Specimens shipped					
		RDX wt, %	NWC various tests	WSU fracto- emission	PSU burn rates	Lockheed SAX <sup>a</sup>	Lockheed acoustic studies
BLX-1	R45M/IPDI	75.5 <sup>b</sup>	+ <sup>c</sup>	+	+	+	+
BLX-2	R45M/IPDI	80.0	+	+	+	+	+
BLX-3	R45M/IPDI	75.0	+	+	+	+	+
BLX-4	GAP/TMETN <sup>d</sup> (1:3)	74.8	+	+	+	+	+
BLX-5 <sup>e</sup>	Acrylic polymer	72.5	-	-	-	-	-
BLX-6 <sup>f</sup>	Acrylic polymer	72.5	+	+	+	+	+
BLX-7 <sup>f</sup>	GAP	68.6	-	-	-	-	-
BLX-8	GAP	68.6	+	+	+	+	+
BLX-9	GAP/BTTN <sup>g</sup> (1:2)	65.9	+	+	+	+	+
BLX-10 <sup>h</sup>	BAMO/THF (1:2)	66.3	-	-	-	-	-
BLX-11 <sup>i</sup>	R45M/IPDI	75.0	-	-	-	-	+

<sup>a</sup>Small angle X-ray.<sup>b</sup>Large particles.<sup>c</sup>+ Sent for testing; - not sent for testing.<sup>d</sup>Metriol trinitrate.<sup>e</sup>Small hand mix.<sup>f</sup>System gelled before it could be cast.<sup>g</sup>Butanetriol trinitrate.<sup>h</sup>Plasticizer exuded from cured formulation.<sup>i</sup>Special mix for acoustic studies.



TABLE 2. Composition of R45M/IPDI Formulations.

Material	Weight percent			
	BLX-1	BLX-2	BLX-3	BLX-11
R45M	23.20	18.55	23.20	23.20
IPDI	1.74	1.39	1.74	1.74
Triphenyl bismuth	0.03	0.03	0.03	0.30
Octanoic acid	0.03	0.03	0.03	0.30
RDX (class A)	22.56	0.00	0.00	0.00
RDX (screened class A)	0.00	32.00	30.00	30.00
RDX (class E)	52.50	48.00	45.00	45.00
Total RDX	75.00	80.00	75.00	75.00
NCO/OH <sup>a</sup>	0.95	0.95	0.95	0.95
Shore A hardness	58.00	65.00	63.00	...

<sup>a</sup>Isocyanate/hydroxyl ratio.

TABLE 3. Composition of GAP Formulations.

Material	Weight percent			
	BLX-4	BLX-7	BLX-8	BLX-9
GAP	4.95	26.73	26.72	9.18
N-100 <sup>a</sup>	1.30	4.68	4.68	2.09
TMETN	18.70	0.00	0.00	0.00
BTTN	0.00	0.00	0.00	22.63
Plasticizer/polymer	3.00	0.00	0.00	2.00
RS-5 <sup>b</sup>	0.00	0.00	0.00	0.20
T-12 <sup>c</sup>	0.005	0.005	0.005	0.005
Octanoic acid	0.00	0.00	0.05	0.00
RDX (screened class A)	44.91	27.43	27.43	39.54
RDX (class E)	29.94	41.15	41.15	26.36
Total RDX	74.80	68.60	68.60	65.90
NCO/OH	1.50	1.00	1.00	1.30
Shore A hardness	12.00	...	70.00	48.00

<sup>a</sup>Poly functional isocyanate.<sup>b</sup>Nitrocellulose.<sup>c</sup>Dibutyltin dilaurate.

TABLE 4. Composition of Acrylic Formulations.

Material	Weight percent BLX-5 and -6
EHA <sup>a</sup>	11.34
VP <sup>b</sup>	7.61
DOM <sup>c</sup>	8.11
TGDMA <sup>d</sup>	0.10
COAA <sup>e</sup>	0.03
t-BPB <sup>f</sup>	0.29
RDX (screened class A)	29.01
RDX (class E)	43.51
Total RDX	72.51
NCO/OH	1.20
Shore A hardness	18.00

<sup>a</sup>2-ethylhexylacrylate.<sup>b</sup>N-vinyl-2-pyrrolidane.<sup>c</sup>Diethylmaleate.<sup>d</sup>Triethyleneglycol dimethacrylate.<sup>e</sup>Cobaltous acetylacetonate.<sup>f</sup>Tertiary-butyl perbenzoate.

TABLE 5. Composition of BAMO/THF Formulations.

Material	Weight percent BLX-10
BAMO/THF (5L)	9.90
N-100	1.25
BTN	22.29
Plasticizer/polymer	2.00
RS-5	0.20
T-12	0.003
Octanoic acid	0.030
RDX (screened class A)	26.53
RDX (class E)	39.80
Total RDX	66.33
NCO/OH	0.95

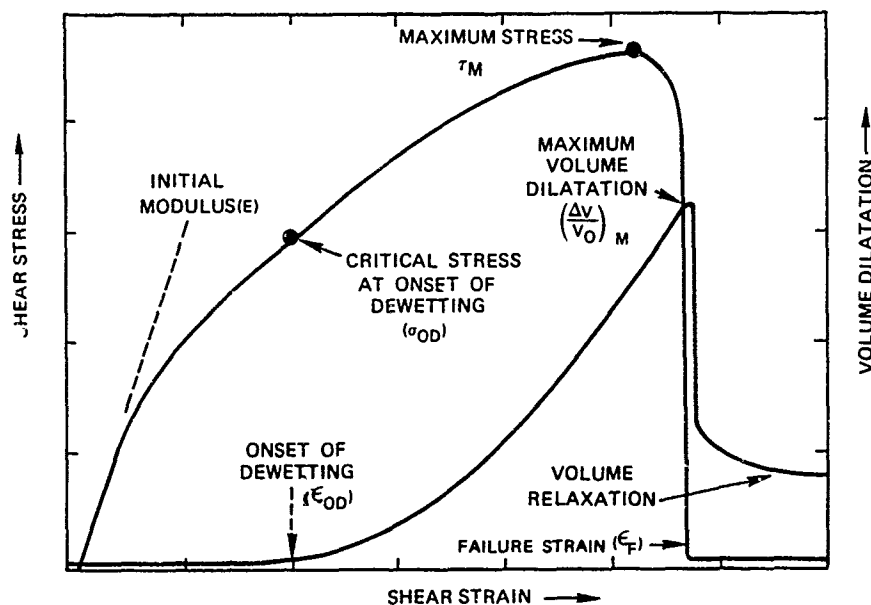


FIGURE 1. Typical Shear Deformation.

properties of interest are the stress and strain at the onset of dewetting ( $\sigma_{OD}$ ,  $\epsilon_{OD}$ ), initial modulus ( $E$ ), maximum stress ( $\sigma_M$ ), strain at failure ( $\epsilon_F$ ), and the maximum dilatation.

The initial part of all the stress-strain curves from the tensile deformation and from the torsional shear deformation overlap quite well. However, the curves begin to diverge as the strain increases past the onset of dewetting.

The tensile and torsional shear data are given in Tables 6 and 7. There is a large variation in modulus values which range from 0.4 to 40.6 MPa.

Both BLX-4 and -6 have very low moduli compared with the other mixes. The BLX-4 contains a large amount of plasticizer while the BLX-6 contains none. It is surprising that the tensile properties of these two mixes are comparable (except for the dilatation) while their shear properties are not. There is no good explanation for this at the present time.

#### THE ONSET OF DEWETTING

The onset of dewetting is of special interest for correlating surface properties and mechanical properties. In the binder system being studied, we assume that the cohesive energy of the binder is larger than the adhesive energy between the binder and the energetic solids.

TABLE 6. Tensile Properties of Baseline Mixes.

Mix No.	E, MPa	$\epsilon_{OD}^a$ , cm/cm	$\sigma_{OD}$ , MPa	$\epsilon_F$ , cm/cm	$\sigma_M^b$ , MPa	$(\Delta V/V_o)_M$ , %
BLX-1	12.8	0.06	0.64	0.13	0.86	3.3
BLX-2	22.4	0.05	0.84	0.09	1.12	1.3
BLX-3	15.9	0.06	0.71	0.13	0.95	3.1
BLX-4	1.5	0.20	0.18	0.22	0.18	0.6 <sup>d</sup>
BLX-6	1.4	0.21	0.13	0.52	0.18	...
BLX-8	40.6	0.04	0.77	0.05	0.90	1.1
BLX-9	8.2	0.06	0.31	0.10	0.40	0.7

<sup>a</sup>0.1% dilatation.<sup>b</sup>Maximum stress.<sup>c</sup>Maximum dilatation (change in volume divided by the original volume).<sup>d</sup>Very large--off scale.

TABLE 7. Shear Properties of Baseline Mixes.

Mix No.	E, <sup>a</sup> MPa	$\epsilon_{OD}^b$ , cm/cm	$\sigma_{OD}$ , MPa	$\epsilon_F$ , cm/cm	$\sigma_M$ , MPa	OV/V <sub>M</sub> , %
BLX-1	16.2	0.06	0.65	0.09	0.86	3.6
BLX-2	25.3	0.06	0.92	0.19	1.24	7.8
BLX-3	16.0	0.07	0.66	0.21	0.98	7.7
BLX-4	1.4	0.20	0.14	0.41	0.17	2.2
BLX-6	0.4	0.34	0.09	1.10	0.19	710.0
BLX-8	31.5	0.03	0.86	0.12	1.41	11.5
BLX-9	9.0	0.07	0.39	0.20	0.68	2.3

<sup>a</sup>The modulus E is obtained by multiplying the shear modulus by 3.<sup>b</sup>The shear strain was converted in order to be comparable to tensile strain by dividing by 3.

Therefore, if an increasing stress is introduced into the composite, the weakest bond will break first. The weakest bond in this case is the binder-solid adhesion. The onset of dewetting is selected to be the point where the volume dilatation reaches 0.1%. As a consequence, the stress at the onset of dewetting should correspond to the energy required to separate the binder-solid interface. For example, the tensile stress at the onset of dewetting is 0.64 and 0.71 MPa for BLX-1 and BLX-3, respectively. The interfacial bonds are the same for both, but BLX-1 contains larger solid particles which are more easily dewetted. The tensile stress at the onset of dewetting for BLX-3 and BLX-8 are 0.71 and 0.77 MPa, respectively. The works of adhesion between the binder and solid RDX for these two mixes, calculated to be 80 and 82 dyns/cm<sup>2</sup> (Reference 8). The work of adhesions and stress at the onset of dewetting change in the same direction. A suitable model for this correlation is still being sought. (This point will be discussed in the next section.)

The effect of plasticizer in the GAP mixes can be seen at the onset of dewetting data. The plasticizer to binder ratios for BLX-8, BLX-9 and BLX-4 are 0, 2, and 3, respectively. As would be expected,  $\epsilon_{OD}$  increases while  $\sigma_{OD}$  decreases as the plasticizer content increases. Thus, increasing the plasticizer concentration results in more plastic flow and lower stress build-up in the composites.

#### BOND ENERGY AND ONSET OF DEWETTING

D. W. Nicholson derived an equation relating the critical radius for detachment under constant stress (Reference 12).

$$r_o \geq r^* = \frac{W E 4(1 + \nu)}{3\sigma^2 3(1 - \nu)^2}$$

where

$r_o$  = radius of spherical inclusion

$r^*$  = critical inclusion radius

$W$  = energy absorbed in debonding

$\sigma$  = stress

$E$  = elastic modulus

$\nu$  = Poisson's ratio

If the onset of dewetting is assumed to be associated with the beginning of breaking of the adhesive bond between RDX and binder, the above equation can be rearranged to

$$E = Kr^*W\sigma^2$$

where  $K$  is a constant and  $\sigma$  would be the stress at the onset of dewetting ( $\sigma_{OD}$ ).

The Poisson's ratio and radius of inclusion are assumed to be constant for the different binders containing the same volume percent of RDX of similar size distribution.

Since the particle sizes are left constant,  $r^*$  can be included in the constant  $K$ . Thus, if the  $\sigma$  values are plotted against  $\sigma_{OD}^2$ , the slope should be proportional to  $W$ . Such a plot for the model mixes is shown in Figure 2 and includes both the tensile and shear data. The fact that all of the points belonging to the hydroxy-terminated polybutadiene (HTPB) mixes fall on a straight line means that the amount of energy absorbed in debonding RDX from binder is the same for all of the HTPB mixes. A good check for the equation that was given previously is that the points are all on a straight line. The slope for the GAP mixes is slightly higher. The magnitude of the difference is not critical at the present time. At least the direction is correct ( $W_{GAP} > W_{HTPB}$ ).

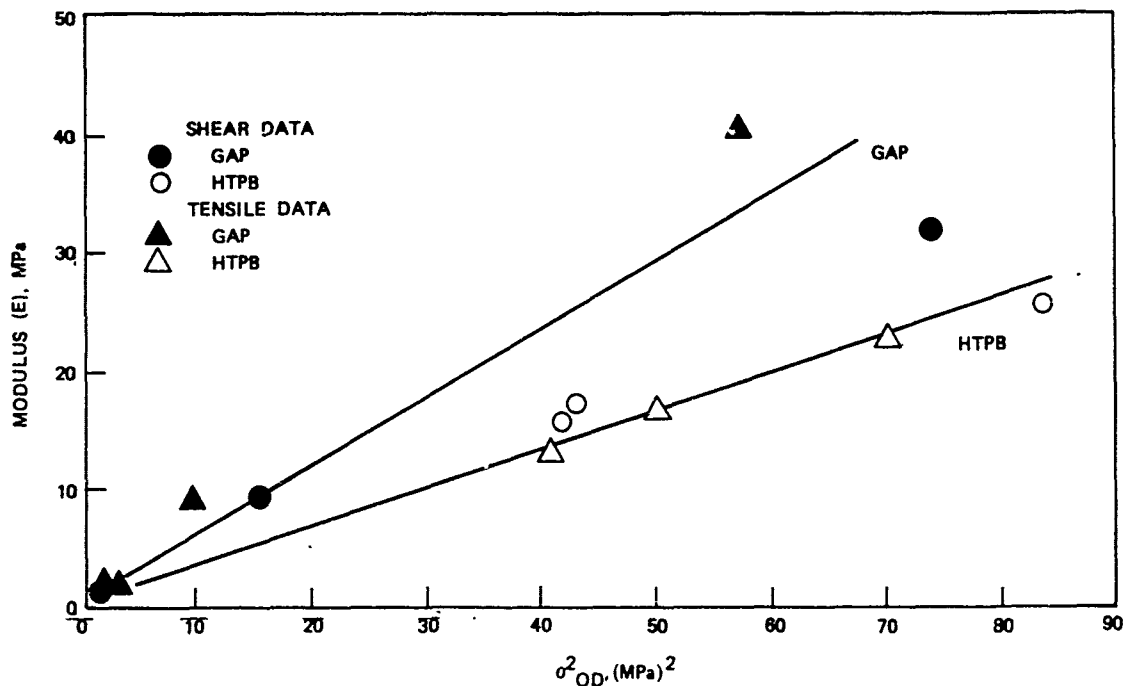


FIGURE 2. Determination of Debonding Energy for GAP and HTPB Mixes.

## FRACTURE TOUGHNESS

The resistance to crack propagation in a material is characterized by the material's fracture toughness (References 13 through 15). The sample configuration for the crack opening mode (tersile deformation) is shown in Figure 3. At the onset of unstable crack propagation the fracture toughness or stress intensity factor,  $K_{IC}$ , is a constant and is given by the equation

$$K_{IC} = \sigma_M (\pi a)^{1/2} F(a/b)$$

where  $\sigma_M$  is the maximum stress and  $a$  and  $b$  are defined in Figure 3. It is an important parameter when describing the mechanical properties of a material because it characterizes the ultimate strength when flaws are present. The stress intensity factors are shown in Table 8.

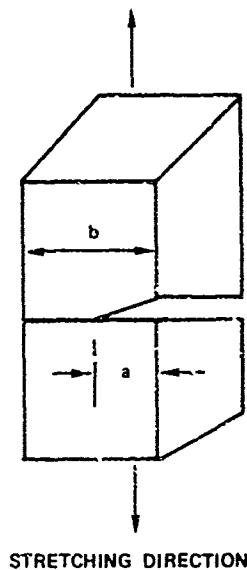


FIGURE 3. Opening Mode Fracture Toughness.

TABLE 8. Stress Intensity Factors  
( $K_{IC}$  ( $K^a P^b m^c$ ))

Sample	BLX-1	BLX-2	BLX-3	BLX-4	BLX-6	BLX-8	BLX-9
$K_{IC}$	87.0	86.2	67.9	16.2	11.1	45.0	27.2

<sup>a</sup>Constant.<sup>b</sup>Pascal.<sup>c</sup>Mass.

## SPECIFIC HEAT DETERMINATION

The DSC module in a DuPont 1090 thermal analyzer was used to determine the specific heats of the formulations. The specific heat of a test specimen is determined by comparing the thermal lag between sample and reference systems under "blank" and "sample" conditions. The blank condition is having aluminum pans of similar weight on the reference and sample probes. The reference system is a piece of sapphire of known weight and specific heat. The thermal lag of the sapphire at different temperature intervals is obtained by subtracting the blank readings from the reference reading with the sapphire in the aluminum pan on the sample probe. The thermal lag of the sample at different temperature intervals is obtained similarly using the sample in place of the sapphire.

The specific heat of the formulations at various temperatures are plotted in Figure 4. The slope change of BLX-4 and BLX-9 are probably associated with the thermal behavior of the energetic plasticizer.

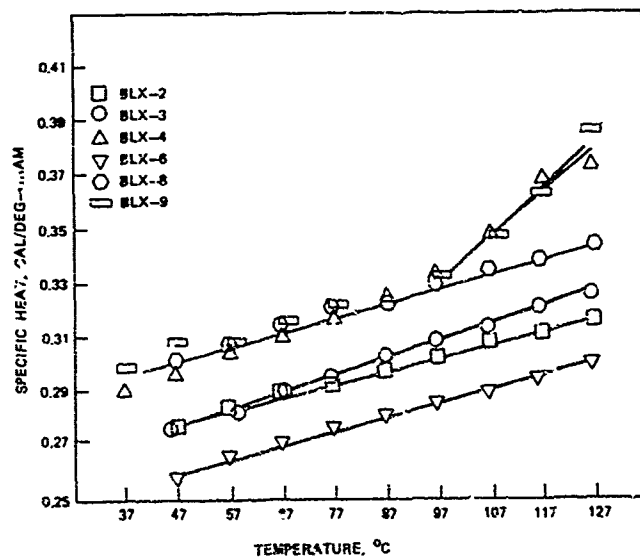


FIGURE 4. Specific Heat of Formulations.



GLASS TRANSITION TEMPERATURE ( $T_g$ )

The glass transition temperature of the model mixes were determined from their low-temperature DSC curves obtained at heating rates of 10°C/min as shown in Table 9.

TABLE 9. Glass Transition Temperature of Model Mixes.

	BLX-1	BLX-2	BLX-3	BLX-4	BLX-6	BLX-8	BLX-9
$T_g$ (°C)	-72	-75	-72	-58	<-100	-40	-65

The plasticized mixes (BLX-4 and -9) show lower glass transition temperature than the unplasticized GAP mix (BLX-8). The glass transition temperature of BLX-6 is very low.

## BURN RATES AND IGNITABILITY

The burn rates of the model mixes are plotted in Figure 5. The data for each binder form separate groups. The GAP mixes containing energetic plasticizer have the highest burn rates. We realize that the low values are caused by an insufficient amount of oxidizer in the mixes of acrylic and HTPB. However, the data will be incorporated into the data matrix for comparison with other data base systems.

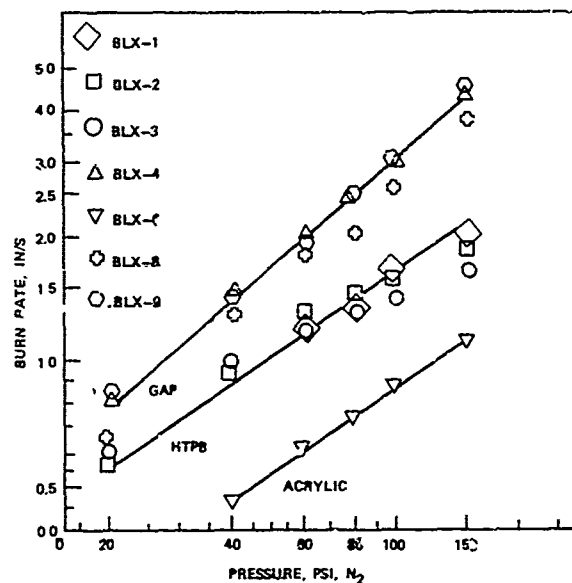


FIGURE 5. Burn Rates of Model Mixes.

The results of the ignition studies are shown in Table 10 (Reference 15). The first column provides the energy flux values of the laser to which the samples were subjected. Under each mix, the left hand column lists values of time in milliseconds (ms) to detect first light which is an indication of first gasification of the sample. The right hand column gives the exposure time for 50% go/no go ignition (go means that the sample will sustain combustion after the laser stimulus is removed.)

A reversal occurs in ignition time at high flux levels (150 to 250 cal/m<sup>2</sup>-s) for the plasticized GAP mixes (BLX-4 and -9). This matter will be investigated as more data are collected. No data are shown for BLX-6 and BLX-8 because there is no ignition at low flux levels and ignition only occurs for BLX-8 at high flux levels. This lack of ignition at low flux levels suggests that the formulation may be candidates for insensitive energetic system.

#### SENSITIVITY

The sensitivity data for the model formulations are still being collected. The drop weight impact sensitivity of the RDX model mixes is shown in Table 11. The mixes with HTPB binder (BLX-1, -2, and -3) and the mix with the acrylic binder (BLX-6) are the least sensitive. The greater sensitivity of BLX-4 and BLX-9 compared with that of BLX-8 (GAP without binder) reflect the effect of energetic plasticizers on the drop weight impact sensitivity of a mix.

Two interesting phenomena have been observed in attempts to compare drop weight impact sensitivity of original and damaged materials. The first one is that some damaged materials become more sensitive but the effect decreases with time due to relaxation. This suggests a healing effect. There also appears to be a directional effect on sensitivity. Preliminary data suggests that materials damaged by uniaxial tension appear to have different sensitivities if tested normal or parallel to the tension direction. However, the data obtained to date for both observations are scattered and experiments are being designed to investigate these observations. One of the difficulties encountered in using the model formulations is that the amount of sample is limited. A large amount of each type of material is required for the scheduled studies. To investigate these observations will require the preparation of a special mix or use of an existing propellant.

#### SPECIFIC IMPULSE ( $I_{sp}$ ) OF MODEL MIXES

While the hazardous properties of the model mixes are being compared, it is also important to have some idea of their performance. One of the performance properties is the specific impulse. The specific impulse of the formulations were calculated and are listed in

TABLE 10. Ignition Time (ms).

Energy flux of laser	Sample									
	BLX-1		BLX-2		BLX-3		BLX-4		BLX-9	
	1st Lt	Go/No Go	1st Lt	Go/No Go	1st Lt	Go/No Go	1st Lt	Go/No Go	1st Lt	Go/No Go
cal/m <sup>2</sup> -s										
60	15.91 ±0.5	18.2 ±0.6	10.4 ±0.5	10.5 ±0.0	11.3 ±0.2	11.75 ±0.2	10.3 ±0.3	11.5 ±0.0	8.9 ±0.6	9.9 ±0.3
100	6.1 ±0.5	10.3 ±0.9	5.0 ±0.6	4.7 ±0.6	5.1 ±0.2	6.75 ±0.2	5.1 ±0.2	5.75 ±0.2	4.2 ±0.5	5.1 ±0.3
150	2.4 ±0.2	5.42 ±0.7	2.4 ±0.2	3.75 ±1.8	3.1 ±0.4	6.5 ±0.9	2.4 ±0.1	4.7 ±1.2	1.5 ±0.4	3.4 ±1.1
200	1.13 ±0.1	4.5 ±0.9	1.2 ±0.1	2.94 ±0.9	1.5 ±0.3	4.6 ±0.5	1.5 ±0.3	8.0 ±1.0	0.6 ±0.3	6.1 ±0.3

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TABLE 11. Drop Weight Impact Sensitivity of RDX Model Mixes.

Mix	Binder	50% height (cm)
BLX-1	25% HTPB (coarse RDX)	46
BLX-2	20% HTPB	37
BLX-3	25% HTPB	52
BLX-4	27.2% (TMETN and GAP)	24
BLX-6	27.5% Acrylic polymer	54
BLX-8	31.4% GAP	37
BLX-9	34.1% (BTTN and GAP)	25

Table 12 (Reference 16). The GAP formulations have the highest specific impulses. The large difference between the specific impulse of BLX-3 and BLX-4 is caused by the higher energies of GAP and TMETN. The specific impulse and hazardous properties of BLX-3 and -4 are compared in Table 13.

TABLE 12. Specific Impulses of Hypothetical RDX Model Mixes.

Mix	Ingredients	I <sub>SP</sub>
BLX-1	25% HTPB	214
BLX-2	20% HTPB	219
BLX-3	25% HTPB	214
BLX-4	27.2% (TMETN and GAP)	258
BLX-8	31.4% GAP	234
BLX-9	34.1% (BTTN and GAP)	256

TABLE 13. Performance of Hazardous Properties.

	BLX-3	BLX-4
Composition	75% RDX plus 25% HTPB	73.8% RDX plus 27.2% (TMETN plasticized GAP)
I <sub>SP</sub>	214	258
Time to ignition under 100 cal/m <sup>2</sup> -s energy flux	5.1 ms	5.1 ms
Drop weight impact (cm)	52	24

A large difference exists between the specific impulse of the BLX-3 and BLX-4, but their times to ignition are similar. If BLX-4 is used instead of BLX-3, the system would gain a lot of energy and sensitivity towards heat. However, BLX-4 is much more impact sensitive. This approach shows the need to collect a variety of data to characterize the system better.

The effect of different binders and energetic plasticizers are better illustrated in the specific impulse values of some hypothetical mixes as shown in Table 14. In these mixes, the RDX is 75% by weight and the binder is 25% by weight. Thus, the values in the first column reflect the different energies of the binders. In the plasticized mixes, the binder consists of two parts of energetic plasticizer to one part of polymer. The BTTN is more energetic than the TMETN plasticizer. The effect of energetic plasticizer is more pronounced in the HTPB system as shown by the large difference in specific impulse between the original and plasticized mixes.

TABLE 14. Effect of Energetic Plasticizer On Specific Impulse of Model Mixes.

Binder	No plasticizer	TMETN: <sup>a</sup> binder	BTTN: <sup>a</sup> binder
HTPB	207	232	237
GAP	233	253	257
BAMO/THF	223	249	253

<sup>a</sup>Ratio = 2:1.

#### SURFACE ANALYSIS OF NEW POLYMER

A new thermoplastic elastomer (TPE) was received from Dr. G. Manser (Morton Thiokol, Wasatch Division, Brigham City, Utah). Thin films of this polymer were prepared from a dilute solution of the polymer in a mixture of methyl isobutyl ketone and ethyl acetate. These thin films were used in surface free energy determinations that were done by a method similar to that of Kaelble (References 17 and 18) and discussed in more detail in a previous report (Reference 8). The equations are shown in Table 15. When  $W_a/2\alpha_e$  is plotted against  $\beta_e/\alpha_e$  as shown in Figure 6, a straight line is obtained, the slope of which lies between that for BAMO/THF and GAP. The following surface free energy terms were used for this polymer:

$$\alpha_s = 5.7$$

$$\gamma_s^D = 32.5$$

$$\beta_s = 2.43$$

$$\gamma_s^P = 5.9$$

$$\gamma_s = 32.5 + 5.9 = 38.4$$

$$\gamma_s^P / \gamma_s = 0.45$$

$$W_a = 85.4 \text{ ergs/cm}^2$$

TABLE 15. Kaelble's Surface  
Free Energy Analysis.

$$\gamma_{lv} = \gamma_{lv}^D + \gamma_{lv}^P = \alpha_l^2 + \beta_l^2$$

$$\gamma_{sv} = \gamma_{sv}^D + \gamma_{sv}^P = \alpha_s^2 + \beta_s^2$$

$$W_a = \gamma_{lv}(1 + \cos \theta)$$

$$W_a = 2(\alpha_l \alpha_s + \beta_l \beta_s)$$

$$\frac{W_a}{2\alpha_l} = \alpha_s + \beta_s (\beta_l / \alpha_l)$$

where

v = vapor

l = liquid

s = solid

$\gamma^D$  = dispersive surface free energy

$\gamma^P$  = polar surface free energy

$\gamma$  = total surface free energy

$W_a$  = work of adhesion

P = polar component

D = dispersive component

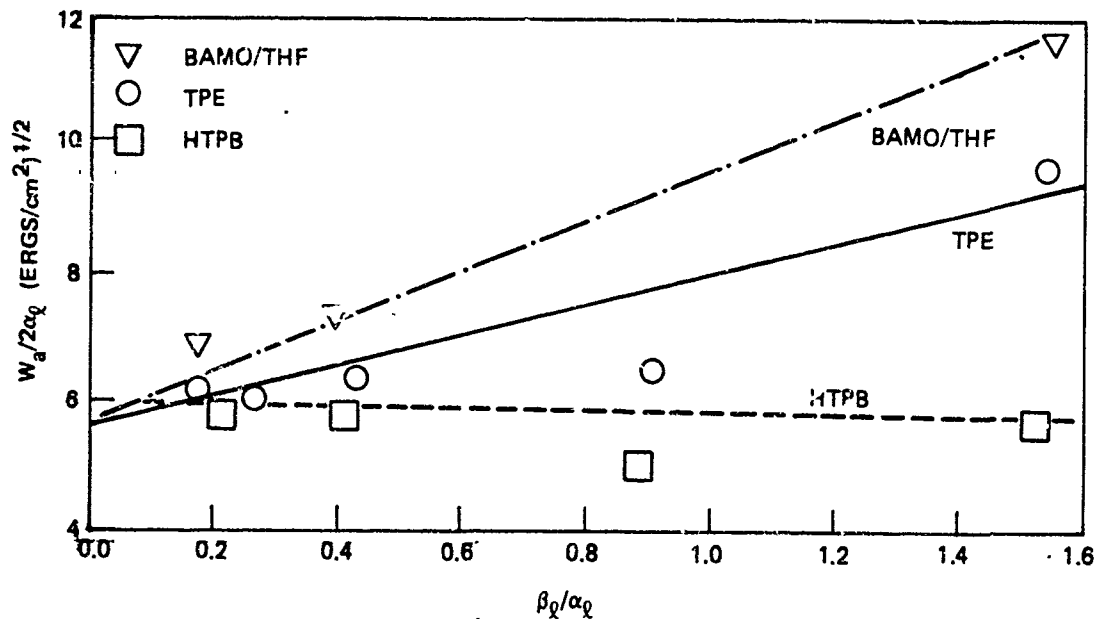


FIGURE 6. Surface Analysis of Thiokol's Thermoplastic Elastomer.

The location of this polymer in the surface energy diagram is shown in Figure 7. According to this analysis, it is a better binder for RDX than GAP or R45M, but not as good as BAMO/THF.

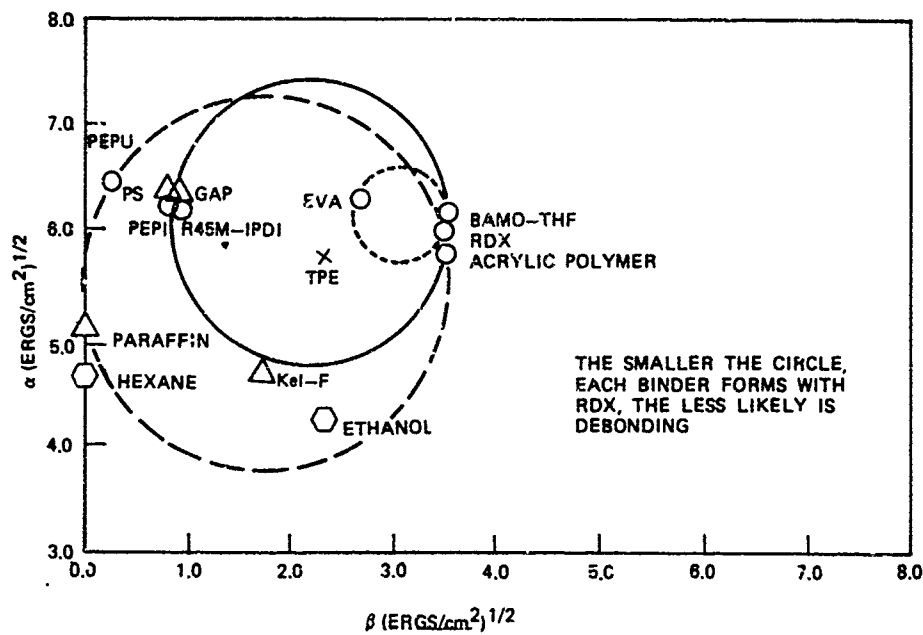


FIGURE 7. Surface Energy Diagram.

CONCLUSIONS

Eight major RDX model formulations have been prepared from three of the baseline binders. Specimens of various configurations were cut and distributed to different investigators.

Results from these investigators are presented for the determinations of surface, mechanical, thermal, burning, sensitivity, and performance characteristics of the formulations.

A method has been found to correlate surface interactions and mechanical properties by means of the onset of dewetting.

Some effect of mechanical damage on impact sensitivity has been observed. It is being investigated further.

When performance and hazardous properties (impact and ignition) are compared, there is an indication that several of the GAP formulations may be classified as insensitive energetic systems.



## GLOSSARY

ARCO	Atlantic Richfield Co., Philadelphia, Pa.
BAMO/THF	bis(azido)methyloxitane/tetrahydrofuran
BTBN	butanetriol trinitrate
COAA	cobaltous acetylacetonate
DOM	dioctyl maleate (2-ethylhexyl isomer)
E	initial modulus
EHA	2-ethylhexyl acrylate
$E_M$	maximum stress
EVA	ethyl vinyl acetate
1st. Lt.	time in ms to detect first light which is an indication of first gasification of the sample
GAP	poly (glycidyl azide)
HMX	cyclotetramethylenetetramine
HTPB	hydroxy terminated polybutadiene
IPDI	isophorone diisocyanate
$I_{SP}$	specific impulse
$K_{IC}$	stress intensity factors
N-100	dismodur N-100; a polyfunctional isocyanate from Mobay Chemical Corporation, Pittsburgh, Pa.
NCO/OH	isocyanate hydroxyl ratio
PBX	plastic bonded explosive
$r_o$	radius of spherical inclusion
$r^*$	critical inclusion radius
R45M	ARCO made HTPB
RS-5	nitrocellulose
RDX	cyclotrimethylenetrinitramine
SAX	small angle X-ray
$\epsilon_F$	strain at failure
$\epsilon_{OD}$	strain at onset of dewetting

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t-BPB	tertiary-butyl perbenzoate
T <sub>g</sub>	glass transition temperature
TGDMA	triethylene glycol dimethacrylate
TMETN	metriol trinitrate
T-12	dibutyltin dilaurate
TPE	thermal plastic elastomer
VP	N-vinyl-2-pyrrolidone
W	energy absorbed in debonding
W <sub>a</sub>	work of adhesion
$\alpha_s$	$\sqrt{\gamma_s^D}$
$\beta_s$	$\sqrt{\gamma_s^P}$
$\gamma_s$	total solid surface free energy
$\gamma_s^D$	dispersive solid surface free energy
$\gamma_s^P$	polar solid surface free energy
$\sigma_{OD}$	stress at onset of dewetting
$\sigma_M$	maximum stress
	Poisson's ratio

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